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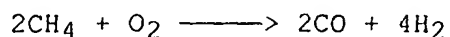
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<p>(21) International Application Number: PCT/EP98/00814</p> <p>(22) International Filing Date: 12 February 1998 (12.02.98)</p> <p>(30) Priority Data: 97200439.4 14 February 1997 (14.02.97) EP (34) Countries for which the regional or international application was filed: AT et al.</p> <p>(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).</p> <p>(72) Inventors: JACOBS, Ludovicus, Leonardus, Gerardus; Badhuisweg 3, NL-1031 CM Amsterdam (NL). LEDNOR, Peter, William; Badhuisweg 3, NL-1031 CM Amsterdam (NL). SEARCY-ROBERTS, Katherine; Badhuisweg 3, NL-1031 CM Amsterdam (NL). VAN DER ZWET, Gerardus, Petrus; Badhuisweg 3, NL-1031 CM Amsterdam (NL).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: CATALYTIC PARTIAL OXIDATION OF HYDROCARBONS</p> <p>(57) Abstract</p> <p>A process for the catalytic partial oxidation of a hydrocarbon feedstock, which process comprises contacting a mixture of the feedstock and an oxygen-containing gas, which mixture has an oxygen-to-carbon ratio in the range of 0.3 to 0.8, at a temperature of at least 750 °C, preferably at least 800 °C, and at elevated pressure with a catalyst comprising a metal selected from Group VIII of the Periodic Table supported on a refractory oxide having at least one cation, characterised in that the refractory oxide comprises cerium as a further modifying cation present in an effective performance-enhancing amount, and a process for the preparation of the catalyst, and a novel catalyst.</p>		

- 1 -

CATALYTIC PARTIAL OXIDATION OF HYDROCARBONS

The invention relates to the preparation of carbon monoxide and/or hydrogen by the catalytic partial oxidation of hydrocarbon feedstocks as methane, natural gas or associated gas.

5 The partial oxidation of hydrocarbons in the presence of a catalyst is an attractive route for the preparation of synthesis gas, mixtures of carbon monoxide and hydrogen. The partial oxidation of hydrocarbons is a highly exothermic reaction and, in
10 the case of methane as hydrocarbon, proceeds by the following reaction:



The optimum catalytic partial oxidation process for application on a commercial scale would give high yields of carbon monoxide and hydrogen at elevated
15 pressures, for example about 30 bar, and high space velocities, for example of the order of 1,000,000 Nl/kg/h or more. For thermodynamic reasons, in order to obtain high yields of carbon monoxide and hydrogen under these process conditions, it is
20 necessary to operate the partial oxidation process at high temperatures.

The literature contains a number of documents disclosing details of experiments conducted into the catalytic partial oxidation of hydrocarbons, in
25 particular methane, employing a wide range of catalysts. The majority of these experiments, however,

- 2 -

have been conducted under very mild conditions or under conditions wholly unsuited to the operation of a commercial catalytic partial oxidation process.

Thus, United States Patent No. 5,149,464 is
5 directed to a method for selectively oxygenating methane to carbon monoxide and hydrogen.

The process described in US-A-5,149,464 is operated at a temperature in the range of from 650 °C to 900 °C, with a range of from 700 °C to 800 °C being preferred:
10 A range of experiments are described in US-A-5,149,464 in which a variety of catalysts comprising Group VIII metals were tested.

A similar general disclosure of a catalyst for use in the catalytic partial oxidation process is made in
15 WO 92/11199. WO 92/11199 specifically discloses experiments in which catalysts comprising iridium, palladium, ruthenium, rhodium, nickel and platinum supported on alumina were applied. All the experiments were conducted under mild process conditions, with
20 typical conditions being a pressure of 1 atmosphere, a temperature of 1050 K (777 °C) and a gas hourly space velocity of about 20,000 hr⁻¹.

WO 93/01130 discloses a process for the partial oxidation of methane using a catalyst comprising a
25 platinum group metal and/or metal oxide supported on a lanthanide oxide, and/or an oxide of a metal from Group IIIB and/or an oxide of a metal from Group IVB of the Periodic Table and/or alumina. The experiments were conducted at a temperature of 750 °C and a gas hourly
30 space velocity of 5000 hr⁻¹ using a feed composition of 45% methane : 5% oxygen : 55% argon. No operating pressure is specified in WO 93/01130. The results disclosed in WO 93/01130 show that, under the operating

- 3 -

conditions selected, catalysts comprising carriers consisting of an oxide of a metal from Groups IIIB or IVB of the Periodic Table, aluminium and the lanthanide cerium exhibited a high selectivity to carbon monoxide.

5 In contrast, the results also show that catalysts comprising as carrier samarium oxide, silica and the mixed oxides of barium/cerium and strontium/cerium exhibited only very poor selectivities to carbon monoxide, instead producing large quantities of carbon
10 dioxide.

As mentioned hereinbefore, an important commercial process is the preparation of mixtures of carbon monoxide and hydrogen, which mixture is then used as the feedstock for a hydrocarbon or organic chemical
15 synthesis process. The catalytic partial oxidation of hydrocarbons is one possible method of carrying out this preparation. However, to be commercially attractive, the process would need to be able to operate at elevated pressures, for example from 30 bara
20 to 150 bara, with very high gas hourly space velocities, for example of the order of 1,000,000 Nl/kg/hr or more. For thermodynamic reasons, in order to obtain the necessary selectivities to carbon monoxide and hydrogen, it is necessary to operate the partial
25 oxidation process at high temperatures. Accordingly, for a partial oxidation process to be viable on a commercial scale, it is essential that the catalyst employed maintains its level of activity and selectivity to the desired products over the prolonged
30 periods of operation demanded of commercial processes.

In European patent application No. 0640561 is disclosed that the catalytic partial oxidation process may be operated under conditions demanded of commercial

processes, in high yield and with low deactivation by employing a catalyst comprising a Group VIII catalytically active metal supported on a refractory oxide having at least two cations selected from Groups IA, IIA, IIIA and IVA of the Periodic Table or the transition metals.

Moreover, in European patent application publication No. 0737164 is disclosed that, when operated under the conditions of elevated pressures and at high temperatures demanded in a commercial process, the catalytic partial oxidation of hydrocarbons can, in the presence of nitrogen, yield a synthesis gas product containing a number of by-products, in particular ammonia (NH_3) and hydrogen cyanide (HCN), in low but significant amounts. It has been found that such by-products can adversely affect downstream processes to convert the carbon monoxide and/or hydrogen produced by the catalytic partial oxidation process, e.g. in the case of Fischer-Tropsch synthesis or in the synthesis of methanol. The presence of by-products, in particular ammonia or hydrogen cyanide, in the products of the catalytic partial oxidation process is thus undesirable.

In European patent application No. 0737164 is disclosed that the generation of such by-products is significantly lower in a process employing a catalyst comprising rhodium, iridium or platinum as catalytically active metal. At such levels it is possible to remove any undesired by-products, using known absorption processes and the like. Alpha-alumina is employed as the catalyst support.

Finally in International patent application publication No. WO 96/04200 is disclosed that catalysts

- 5 -

employed in such catalytic partial oxidation processes at conditions enabling operation on a commercial scale may be subject to thermal shock with resultant damage to the catalyst. In WO 96/04200 is disclosed therefore
5 a process which employs a Group VIII catalytically active metal supported on a zirconia-based carrier comprising oxides of one or more of the rare earth, Group IIIB or Group IIA elements of the Periodic Table, which is found to have a high thermal shock resistance.

10 Accordingly it will be apparent that there are a number of conditions and circumstances which affect the performance of a catalytic partial oxidation reaction, and that whilst it is possible to optimise in terms of individual performance parameters, there is some
15 conflict between individual optimisations, each directed specifically to one of the above performance parameters, whereby it is not possible to operate a process with simultaneous optimisation of all conditions. Specifically, nitrogen is present in many
20 natural gas feedstocks, and the preparation of pure, nitrogen-free oxygen on a commercial scale is both very expensive and technically difficult. Therefore the process must produce acceptably low levels of N-containing by-product. Moreover the choice of
25 catalytically active metal, refractory oxide and the like in the catalyst to be effective on a commercial scale must be made bearing in mind factors including high temperature and pressure resistance and thermal shock resistance under the extreme conditions to be
30 employed in terms of the factors hereinbefore mentioned. Finally the process must produce optimum yields and selectivity to desired products and optimum lifetime under such extreme conditions, and indeed

- 6 -

under varying conditions which may prevail in the event of fluctuations in operation.

Accordingly, there is a need for a process for the catalytic partial oxidation of hydrocarbons in which
5 nitrogen is present during the partial oxidation reactions, which may be applied on a commercial scale to produce a product of carbon monoxide and/or hydrogen in high yield and selectivity, containing a minimum of components such as ammonia and hydrogen cyanide, and at
10 low or negligible catalyst deactivation rates.

Surprisingly, it has been found that, by employing in the catalytic partial oxidation process a catalyst comprising the catalytically active component, supported on a refractory oxide support comprising a
15 performance enhancing modifier, the above objects may be achieved in admirable manner, for a wide range of operating conditions. Low yields of NH_3 and HCN are obtained. The conversion of methane is very high.

Accordingly, in its broadest aspect, the present
20 invention provides a process for the catalytic partial oxidation of a hydrocarbon feedstock, which process comprises contacting a mixture of the feedstock and an oxygen-containing gas, which mixture has an oxygen to carbon ration in the range of 0.3 to 0.8, at a
25 temperature of at least 750 °C, preferably at least 800 °C and at elevated pressure with a catalyst comprising a metal selected from Group VIII of the Periodic Table supported on a refractory oxide having at least one cation, characterised in that the
30 refractory oxide comprises cerium as a further modifying cation present in an effective performance-enhancing amount.

- 7 -

Reference herein to a modifying cation is to a cation which is incorporated in suitable manner in the catalyst thereby modifying the properties thereof. Without being limited to this theory it would seem that the modifying cation is essentially incorporated in the refractory oxide support as distinct from the catalytically active metal containing refractory oxide support, whereby the excellent results obtained are due to the combination of the optimised catalytically active metal portion of the catalyst and of the optimised modified refractory oxide support portion of the catalyst.

It is a particular advantage of the process of the present invention that the nature and amount of the performance-enhancing modifying cation in the refractory oxide support, would seem to be highly specific as is the manner of incorporation therein in modifying rather than mixed-oxide fashion, whereby enhancements in the performance parameters of yield, selectivity, deactivation resistance and low by-product formation are simultaneously apparent. Without being limited to this theory it would seem that a form of co-operation is effective between all of these performance parameters, whereby the enhancement in one parameter serves to generate enhancement in the other parameters.

As hereinbefore mentioned, the products of the process may be subjected in a further stage to a process in which ammonia and/or hydrogen cyanide is removed.

The process of the present invention offers the significant advantage that, owing to the very low amounts of ammonia and hydrogen cyanide produced in the first stage, removal of the undesirable components from the products is a relatively simple operation. This in

- 8 -

turn gives a process which is economical and most attractive for application on a commercial scale.

The process of the present invention may be used to prepare carbon monoxide and/or hydrogen from any gaseous hydrocarbon or hydrocarbon having a low boiling point such that it is gaseous under the conditions prevailing during the partial oxidation reactions. The process is particularly suitable for the partial oxidation of methane, natural gas, associated gas or other sources of light hydrocarbons. In this respect, the term "light hydrocarbons" is a reference to hydrocarbons having from 1 to 5 carbon atoms. The process may be applied in the conversion of naturally occurring reserves of methane which contain a substantial amount of carbon dioxide. The feed preferably comprises methane in an amount of at least 50% by volume, more preferably at least 75% by volume, especially at least 80% by volume.

The hydrocarbon feedstock is contacted with an oxygen-containing gas during the partial oxidation process. Air may be used as the oxygen-containing gas, in which case nitrogen will be present in the feed and reaction mixture in large quantities. Alternatively, the use of substantially pure oxygen may be preferred, in which case nitrogen may be present in much lower, but nevertheless significant, quantities. Typically, the substantially pure oxygen is prepared on a commercial scale by the distillation of liquified air. The amount of nitrogen present in the substantially pure oxygen will depend upon the operating conditions of the air distillation process. It is an advantage of the process of the present invention that the tolerances of the air distillation process may be

relaxed, thereby allowing a greater amount of nitrogen to be present in the substantially pure oxygen being used in the catalytic partial oxidation process. This, in turn, offers advantages in terms of a reduction in the overall capital and operating costs of the air distillation plant. Usually nitrogen may be present in amounts up to 70 vol%, suitably between 1 and 65 vol%, based on the total volume of the mixture of feedstock and oxygen-containing gas.

10 The feed may optionally comprise steam.

 The feed may comprise the hydrocarbon feedstock and oxygen in an amount sufficient to give a suitable oxygen-to-carbon ratio. Preferably, the oxygen-to-carbon ratio is in the range of from 0.3 to 0.8, more preferably from 0.45 to 0.75. References to the oxygen-to-carbon ratio refer to the ratio of oxygen in the form of molecules (O_2) to carbon atoms present in the hydrocarbon feedstock. Preferably, the oxygen-to-carbon ratio is in the range of from 0.45 to 0.70, with oxygen-to-carbon ratios of the stoichiometric ratio, 0.5, that is in the range of from 0.45 to 0.65, being particularly suitable.

 If steam is present in the feed, the steam-to-carbon ratio (that is the ratio of molecules of steam (H_2O) to carbon atoms in the hydrocarbon) is preferably in the range of from above 0.0 to 3.0, more preferably from above 0.0 to 2.0.

 The process of the present invention is operated at elevated pressures, that is pressures significantly above atmospheric pressure. The process may be operated at pressures in the range of up to 150 bara. Preferably, the operating pressure is in the range of

- 10 -

from 5 to 125 bara, more preferably from 10 to 100 bara.

The catalytic partial oxidation process may be operated at any suitable temperature. Under the preferred conditions of high pressure prevailing in the catalytic partial oxidation process, the feed gases are typically allowed to contact the catalyst at elevated temperatures in order to achieve the level of conversion required for a commercial scale operation. Accordingly, the process is typically operated at a temperature of at least 750 °C, preferably at least 800 °C. Preferably, the operating temperature is in the range of from 800 to 1300 °C, more preferably in the range of from 900 to 1200 °C. Temperatures in the range of from 1000 to 1200 °C are particularly suitable.

The feed mixture may be provided during the catalytic partial oxidation process at any suitable gas space velocity. It is an advantage of the process of the present invention that very high gas space velocities may be applied. Thus, typical space velocities for the catalytic partial oxidation process (expressed as normal litres of gas per kilogramme of catalyst per hour) are in the range of from 20,000 to 100,000,000 Nl/kg/hr, more preferably in the range of from 50,000 to 50,000,000 Nl/kg/hr. Space velocities in the range of from 500,000 to 30,000,000 Nl/kg/hr are particularly suitable.

The catalyst employed in the process of the present invention comprises, as active component, a metal selected from Group VIII of the Periodic Table of the Elements supported on a refractory oxide as hereinbefore defined. References in this specification to the Periodic Table of the Elements are to the CAS version,

- 11 -

as published in the CRC Handbook of Chemistry and Physics, 68th Edition. Preferred catalysts for use in the process of the present invention comprise, as the catalytically active component, a metal selected from rhodium, iridium and platinum. As has been discussed hereinbefore, these metals offer the significant advantage that substantially lower amounts of ammonia and hydrogen cyanide are produced during the catalytic partial oxidation reaction, compared with the other metals from Group VIII of the Periodic Table of the Elements. A catalyst comprising rhodium or iridium is a particularly suitable catalyst.

The catalytically active metal may be deposited on the refractory oxide support by techniques well known in the art. A most suitable technique for depositing the metal on the oxide support is impregnation, which technique typically comprises contacting the oxide support with a solution of a compound of the catalytically active metal, followed by drying and calcining the resulting material.

The catalyst may comprise the catalytically active metal in any suitable amount to achieve the required level of activity. Typically, the catalyst comprises the active metal in an amount in the range of from 0.01 to 20% by weight, preferably from 0.02 to 10% by weight, more preferably from 0.1 to 7.5% by weight.

The Group VIII metal is supported on a refractory oxide carrier, which refractory oxide comprises at least one cation. The refractory oxide is preferably a simple or a mixed oxide, consisting of one to three cations respectively. The one or more cations of the refractory oxide support are preferably (each) selected from Groups IA, IIA, IIIA and IVA of the Periodic Table

- 12 -

of the Elements or the transition metals. More preferably, the one or more cations are each selected from Groups IA, IIA, IIIA, IIIB, IVA and IVB and the lanthanides. A preferred catalyst comprises a refractory oxide having at least one cation selected from Groups IA, IIA and IIIB and the lanthanides and at least one cation selected from Groups IIIA, IVA and IVB. More preferably, the catalyst comprises a refractory oxide having at least one cation from Group IIIB and/or Group IVA. Aluminium is a particularly preferred cation selected from Group IIIA. Zirconium is a most suitable cation selected from Group IVA. One most suitable refractory oxide for use as a support in the catalyst is a binary oxide of zirconia and aluminium, in particular in (partially) stabilised form such as ZTA and PSZ (zirconia-toughened alumina, and partially-stabilised zirconia).

A mixed oxide may comprise two or more cations in any desired amounts. For example zirconia and aluminium may be present in any desired amounts, preferably each independently in an amount of 1-99% mass, more preferably in an amount of 1-50% and 50-99% mass respectively, most preferably in an amount of 15-25% and 85-75% mass respectively. The oxide is suitably prepared by techniques as known in the art or is commercially available. For example the mixed oxides ZTA and PSZ are commercially available from Selee Inc and Hi-Tech.

The mixed oxide support may comprise incidental amounts of other cations, present as a result of the synthesis thereof or for functional purpose.

The refractory oxide comprises at least one cation as hereinbefore defined, and additionally comprises

- 13 -

cerium in the form of a modifying cation as herein-
before defined. Preferably cerium is present in an
amount of up to 1.50% by weight based on the total
weight of the oxide support, more preferably of 0.05 to
5 1.25%, most preferably of 0.10 to 0.70%, for example
0.15 to 0.50% such as in the region of 0.25%.

Cerium may be introduced by known means for
modifying refractory oxides, and is preferably intro-
duced by impregnation of the oxide support. Impregna-
10 tion may be of the pure oxide support or of the oxide
support including any other components such as the
catalytically active metal and the like, whereby it may
be carried out simultaneously with, prior or subsequent
to impregnation with any other components as desired,
15 by co- or solo-impregnation. For example the order of
impregnation may depend on a number of factors.
Excellent results are obtained by impregnation, for
example of a ZTA support, with 0.25% cerium modifier
prior to impregnation with 5% iridium as the
20 catalytically active metal.

Preferred techniques for impregnation are by
dipping, painting, spraying, immersing, applying by
measured droplet and the like of a suspension or
solution of the modifying cation, with subsequent
25 drying in hot air or the like and calcining, in manner
that a uniform impregnation is achieved. Preferably
impregnation and/or drying is carried out in the
absence of distorting gravitation, meniscus or
capillary effects during drying, which might provide an
30 undesired gradient or total content of the impregnated
cation. For example the oxide support may be rotated or
suspended in manner that contact with any other objects
does not encourage meniscus or capillary effects.

- 14 -

Additional modifying cations and/or components may be introduced for purposes of chemical and/or physical catalyst property enhancement, using techniques as known in the art.

5 It is however preferred that cerium is introduced as the only modifying cation, and is introduced by solo-impregnation of the oxide support, prior to impregnation of the catalytically active metal.

10 The oxide support may be formed in manner to provide a desired catalyst structure, or may be provided on a further, preferably inert, structure-forming component. Such structure-forming component may be present during the operation of the process or be removed by natural means on start up of the process.

15 For example an oxide support in the form of a ceramic foam, monolith, sieve or the like may be provided together with a structure-forming sponge, template or the like, which is removed by combustion by natural means on start up of the process, according to known

20 techniques.

 Any suitable reaction regime may be applied in the process of the first stage of the present invention in order to contact the reactants with the catalyst. One suitable regime is a fluidised bed, in which the

25 catalyst is employed in the form of particles fluidised by a stream of gas. A preferred reaction regime for use in the process is a fixed-bed reaction regime, in which the catalyst is retained within a reaction zone in a fixed arrangement. Particles of catalyst may be

30 employed in the fixed-bed regime, retained using fixed-bed reaction techniques well known in the art. Alternatively, the fixed arrangement may comprise the catalyst in the form of a monolithic structure. A most

- 15 -

preferred monolithic structure comprises a ceramic foam. Suitable ceramic foams for use in the process are available commercially. Further, alternative forms for the catalyst include refractory-oxide honeycomb monolith structures.

In a preferred embodiment of the process of this invention, the feed is contacted with a catalyst retained in a fixed arrangement, which arrangement has a high tortuosity. The term "tortuosity" is a common term in the art which, when referring to a fixed catalyst bed, can be defined as the ratio of the length of the path taken by a gas flowing through the bed to the length of the shortest straight line path through the bed. Thus, the honeycomb monolith structures have a tortuosity of 1.0. For the purposes of the present invention, the term "high tortuosity" is a reference to arrangements having a tortuosity substantially greater than that of the honeycomb monolith structures, in particular a tortuosity of at least 1.1. A fixed bed of catalyst particles typically has a tortuosity of 1.5, whilst ceramic foams may be prepared having a tortuosity in the range of from 3.0 to 4.0, or even higher. In general, the tortuosity of the fixed-bed arrangement is preferably in the range of from 1.1 to 10.0, more preferably to 5.0. A most suitable range of tortuosity is from 1.3 to 4.0.

It has been found that by employing the catalyst in a fixed-bed arrangement having a high tortuosity allows the required conversion to be achieved with only a relatively very short contact time between the reacting gases and the catalyst. In this way, only a very low volume of catalyst is required, which in turn allows

- 16 -

the very high gas space velocities of the present process to be easily achieved on a commercial scale.

It is a further preferred feature of the process of this invention that the catalyst is retained in the form of a fixed arrangement having a large number of pores. In this respect, the term "pore" is a general reference to a space or interstice in the fixed arrangement between two adjacent portions of the catalyst. Thus, in the case of a fixed bed of catalyst particles, the term "pore" refers to the space between two adjacent particles. When referring to ceramic foams, the term pore refers to the openings or spaces between adjacent portions or lands of the ceramic structure. Thus, it will be appreciated that the pores referred to in respect of the present invention have a nominal diameter of the order of magnitude of 0.1 mm. These are to be contrasted with pores which may be present in the catalyst support material itself, which may be porous.

The fixed arrangement preferably comprises at least 750 pores per square centimetre. More preferably, the fixed arrangement comprises from about 1000 to about 15000 pores per square centimetre, especially from about 1250 to about 10000 pores per square centimetre.

The gaseous mixture of the hydrocarbon feedstock and the oxygen-containing gas is preferably contacted with the catalyst under adiabatic conditions. For the purposes of this specification, the term "adiabatic" is a reference to reaction conditions in which substantially all heat loss and radiation from the reaction zone is prevented, with the exception of heat leaving in the gaseous effluent stream of the reactor.

- 17 -

In a subsequent stage of the process of this invention, the product gases may be subjected to a treatment to remove the low amounts of ammonia and hydrogen cyanide produced in the catalytic partial oxidation process. Suitable processes for removing ammonia and hydrogen cyanide from gaseous streams are known in the art.

For a general discussion of absorption processes and techniques, reference is made to the Chemical Engineer' Handbook, Fifth Edition, edited by R.H. Perry and C.H. Chilton, pages 14-1 to 14-16.

In a further aspect, the present invention relates to carbon monoxide or hydrogen whenever prepared by a process as hereinbefore described.

The mixture of carbon monoxide and hydrogen prepared by the process of this invention is particularly suitable for use in the synthesis of hydrocarbons, for example by means of the Fisher-Tropsch synthesis, or the synthesis of oxygenates, for example methanol. Processes for the conversion of the mixture of carbon monoxide and hydrogen into such products are well known in the art.

In a further aspect, of the invention there is provided a process for the preparation of a catalyst as hereinbefore defined comprising providing a refractory oxide support, optionally having a catalyst structure as herein defined, and providing thereon a metal and modifying cerium cation, as hereinbefore defined. Preferably the modifying cerium cation is provided on the support prior to provision of the metal thereon.

In a further aspect of the invention there is provided a novel catalyst as hereinbefore defined, preferably for use in a catalytic partial oxidation

- 18 -

process as hereinbefore defined. In particular the invention concerns a catalyst comprising a metal selected from Group VIII of the Periodic Table supported on a refractory oxide having at least one cation, characterised in that the refractory oxide comprises cerium as a further modifying cation present in an effective performance-enhancing amount.

The process of the present invention is further described by way of the following illustrative examples.

Example 1

Catalyst Preparation

Zirconia-toughened alumina ceramic foam (65 pores per inch, ex Selee Inc.) was crushed and sieved to 30/80 mesh before placing in an oven at 120 °C overnight. The foam particles were weighed and the amount of iridium chloride solution (138 g/l) needed to give a 5% iridium loading was calculated. The iridium solution was added to the 30/80 mesh particles with mixing and drying in a microwave oven in between. This was repeated until all the necessary amount of solution was added. After this the 30/80 mesh particles were dried and calcined as follows: 4 hours at 120 °C, temperature raised to 700 °C with 80 °C/hour, 4 hours at 700 °C and cool-down to 120 °C.

Cation Modification

The modified catalysts were prepared by adding a solution of cerium nitrate (215 g/l) to the 30/80 mesh ceramic foam particles described above, prior to iridium impregnation. The amount of solution needed was calculated and weighed into a bottle. This was then further diluted in order to obtain a homogeneous impregnation. The diluted cerium solution was added to

- 19 -

the 30/80 mesh particles in stages with mixing and drying in a microwave oven in between. This was repeated until all the necessary solution was added. After this the 30/80 mesh particles were dried and
5 calcined as stated before, except that a slower rate (25 °C/hour) was used to raise the temperature to 700 °C. Subsequently the iridium was added as described above.

The resulting catalysts comprised 5.0% by weight
10 iridium and 0.05, 0.25, 1.25 and 12.2% by weight cerium, based on the total weight of the oxide support.
Catalytic Partial Oxidation

A reactor was constructed comprising a transparent sapphire tube. The modified catalyst prepared as
15 hereinbefore described was crushed and loaded into the sapphire tube and retained in the form of a fixed bed of catalyst particles having a tortuosity of about 1.5. Methane and oxygen, in sufficient amounts to give an oxygen-to-carbon ratio of 0.56 to 0.64, were thoroughly
20 mixed just before being introduced into the reactor to contact the fixed bed of catalyst. The mixture of methane and oxygen was fed to the reactor at a pressure of in the range of 11 to 30 bara and at a gas hourly space velocity (GHSV) in the range of 4,000,000 to
25 4,100,000 Nl/kg/hr (Normal litres, i.e. litres at STP conditions (0 °C and 1 bara), of gas per kilogramme of catalyst per hour). The mixture comprised nitrogen in a similar amount to oxygen.

The adiabatic operating temperature of the catalyst
30 bed, in the range of from 940 °C to 1190 °C, was measured by optical pyrometry. The composition of the gas mixture leaving the reactor was determined by gas

- 20 -

chromatography and weighing water condensed from the gas stream leaving the reactor.

In measuring the following performance parameters it was convenient to select a combination of operating conditions in the selected ranges, given as con-
5 conditions 1, 2 and 3 below, corresponding to greatest performance sensitivity. By this means any inferior performance is immediately apparent.

Condition 1:

10 Pressure 11 bara
CH₄ flow 760 Nl/h
O₂ flow 440 Nl/h (O₂/CH₄=0.58)
N₂ flow 400 Nl/h
GHSV 4.0 x 10⁶ Nl/kg/h
15 Catalyst: 400 mg, 30-80 mesh particles
Adiabatic equilibrium temperature 990 °C

Condition 2:

Pressure 30 bara
CH₄ flow 730 Nl/h
20 O₂ flow 470 Nl/h (O₂/CH₄=0.64)
N₂ flow 400 Nl/h
GHSV 4.0 x 10⁶ Nl/kg/h
Catalyst: 400 mg, 30-80 mesh particles
Adiabatic equilibrium temperature 1190 °C

Condition 3:

25 Pressure 11 bara
CH₄ flow 770 Nl/h
O₂ flow 430 Nl/h (O₂/CH₄=0.56)
N₂ flow 440 Nl/h
30 GHSV 4.1 x 10⁶ Nl/kg/h
Catalyst: 400 mg, 30-80 mesh particles
Adiabatic equilibrium temperature 940 °C

- 21 -

The conversion of methane and the selectivity of the process to carbon monoxide and hydrogen (on the basis of methane converted) were measured for a first set of conditions adapted for low-temperature, non-equilibrium operation (Condition 1). The ammonia content of product gas mixture was measured for a second set of conditions adapted for high-temperature, near-equilibrium operation (Condition 2).

The process was operated for typically 30 hours, and the deactivation in terms of relative loss in methane conversion level was measured after 17 hours at a third set of operating conditions adapted for low-temperature, non-equilibrium operation (Condition 3). The results of the experiment are summarised in the Table I hereinbelow.

Comparative Example

Using the same general procedure as described in Example 1, samples of a barium-modified iridium-containing catalyst were prepared by impregnation of the zirconia-toughened alumina foam/extrudates using an aqueous solution of barium acetate. The resulting catalysts comprised 5.0% by weight iridium, and 0.25, 1.25 and 6.0% by weight barium, based on the total weight of the oxide support.

The thus prepared catalysts were loaded into the apparatus and tested for activity in the catalytic partial oxidation of methane using the same general procedure and operating conditions as described in Example 1.

The gaseous product stream of the catalytic partial oxidation reactor was subjected to an absorption treatment as described in Example 1.

The results of the experiment are summarised in the Table II hereinbelow.

As can be seen from the data set out in the Tables, an effective performance-enhancing amount of modifier can be deduced for the Example 1, however such amount is not apparent for the Comparative Example.

The highly specific nature of the process of the invention can be seen by comparison of the cerium-modified catalyst of Example 1 with the barium-modified catalysts of the Comparative Example, whereby it is apparent that cerium has a performance-enhancing effect as a modifier and also has an optimum effective performance-enhancing amount. Neither observation was apparent for barium, which was not seen to have a performance-enhancing effect as a modifier.

TABLE I

Catalyst No.	1	2	3	4	5
Modifier (%)	0	0.05	0.25	1.25	12.2
CH ₄ conversion (%) ³	86	85	90	82	80
CO selectivity (%) ^{1,3}	94	94	94	93	91
H ₂ selectivity (%) ^{2,3}	86	84	87	88	83
NH ₃ in product (ppmv) ⁴	4.7	3.9	2.9	4.1	>30
Deactivation (%) ⁵	4.4	3.1	2.7	5.7	13.0
¹ selectivity to CO based on CH ₄ conversion					
² selectivity to H ₂ based on CH ₄ conversion					
³ uncertainty approx. 1% (absolute)					
⁴ uncertainty approx 0.5 ppmv					
⁵ uncertainty approx 0.5% (absolute)					

TABLE II

Catalyst No.	1	6	7	8	
Modifier (%)	0	0.25	1.25	6.0 ⁶	
CH ₄ conversion (%) ³	86	87	84	-	
CO selectivity (%) ^{1,3}	94	94	93	-	
H ₂ selectivity (%) ^{2,3}	86	86	87	-	
NH ₃ in product (ppmv) ⁴	4.7	-	4.6	-	
Deactivation (%) ⁵	4.4	4.2	4.7	-	
1 selectivity to CO based on CH ₄ conversion					
2 selectivity to H ₂ based on CH ₄ conversion					
3 uncertainty approx. 1% (absolute)					
4 uncertainty approx 0.5 ppmv					
5 uncertainty approx 0.5% (absolute)					
6 This catalyst could not be ignited					
- not determined					

C L A I M S

1. A process for the catalytic partial oxidation of a hydrocarbon feedstock, which process comprises contacting a mixture of the feedstock and an oxygen-containing gas, which mixture has an oxygen-to-carbon ratio in the range of 0.3 to 0.8, at a temperature of at least 750 °C, preferably at least 800 °C, and at elevated pressure with a catalyst comprising a metal selected from Group VIII of the Periodic Table supported on a refractory oxide having at least one cation, characterised in that the refractory oxide comprises cerium as a further modifying cation present in an effective performance-enhancing amount.
2. A process according to claim 1, characterised in that at least one cation of the refractory oxide support is/are (each) selected from groups IA, IIA, IIIA and IVA of the Periodic Table of the Elements or the transition metals.
3. A process according to claim 1 or claim 2, characterised in that cerium is present in an amount of up to 1.50% by weight based on the total weight of the oxide support, more preferably of 0.05 to 1.25%, most preferably of 0.10 to 0.70%, for example 0.15 to 0.50% such as in the region of 0.25%, and is introduced by impregnation of the oxide support.
4. A process according to any of claims 1 to 3, characterised in that the hydrocarbon feedstock comprises methane, natural gas, associated gas or a source of light hydrocarbons.

- 25 -

5. A process according to any preceding claim, characterised in that the feed is contacted with the catalyst at a pressure in the range of up to 150 bara, preferably from 2 to 125 bara, more preferably from 2 to 100 bara, at a temperature in the range of from 800 to 1300 °C, preferably from 900 to 1200 °C, and at a gas hourly space velocity in the range of from 20,000 to 100,000,000 Nl/kg/hr, preferably from 50,000 to 50,000,000 Nl/kg/hr, more preferably from 500,000 to 30,000,000 Nl/kg/hr.
6. A process according to any preceding claim, characterised in that the catalyst comprises rhodium or iridium.
7. A process according to any preceding claim, characterised in that the catalyst is retained in a fixed arrangement, preferably in the form of a fixed bed of catalyst particles or in the form of a ceramic foam.
8. Process for the preparation of a catalyst comprising a metal selected from Group VIII of the Periodic Table supported on a refractory oxide having at least one cation, wherein the refractory oxide comprises cerium as a further modifying cation present in an effective performance-enhancing amount comprising providing the refractory oxide as the support, optionally having a catalyst structure as herein defined with reference to claim 7, and providing thereon metal and modifying cerium cation.
9. Process according to claim 8 wherein the modifying cerium cation is provided on the oxide support prior to provision of the metal thereon.
10. A novel catalyst as hereinbefore defined with reference to any of claims 1 to 3, 6 and 7, preferably

- 26 -

for use in a catalytic partial oxidation process as
hereinbefore defined with reference to any of claims 1,
4, and 5.